



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 086 444
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 83101193.7

(51) Int. Cl.²: **H 01 F 1/36, G 03 G 9/10,
C 04 B 35/26**

(22) Date of filing: 08.02.83

(30) Priority: 13.02.82 JP 21923/82

(71) Applicant: **TDK ELECTRONICS CO., LTD.**, 13-1,
Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)

(43) Date of publication of application: 24.08.83
Bulletin 83/34

(72) Inventor: Imamura, Kenji c/o TDK Electronics Co., Ltd.,
13-1, Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)
Inventor: Saitoh, Hiroshi c/o TDK Electronics Co., Ltd.,
13-1, Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)
Inventor: Kaidzaki, Katsuhisa c/o TDK Electronics Co.,
Ltd., 13-1, Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)
Inventor: Makino, Motohiko c/o TDK Electronics Co.,
Ltd., 13-1, Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)

(84) Designated Contracting States: **AT BE DE GB IT NL**

(74) Representative: **Wächtershäuser, Günter, Dr.**, Tal 29,
D-8000 München 2 (DE)

(54) **Magnetic carrier powder.**

(57) A magnetic carrier powder composed of ferrite powder particles having a spinel structure and an average particle size of less than 30 µm.

EP 0 086 444 A1

0086444
EA-4147

TDK-209
(870009)

- 1 -

MAGNETIC CARRIER POWDER:

The present invention relates to a magnetic carrier powder. More particularly, the present invention relates to a magnetic carrier powder to be used for magnetic brush development.

Heretofore, as a magnetic carrier powder to be used for magnetic
5 brush development, there has been used an iron powder or a soft ferrite powder and it has been believed that the average particle size of the powder should preferably be from 30 to 1000 μm .

However, such a conventional carrier powder is not totally satisfactory in that it does not provide satisfactory image quality
10 such as a resolving power, graininess, black uniformity or gradation of the image.

Under these circumstances, it is the primary object of the present invention to provide a magnetic carrier powder which is capable of providing an image having an improved image quality
15 such as the resolving power, graininess, black uniformity or gradation.

The present inventors have conducted extensive researches and as a result, have found that the object can be attained by reducing the ferrit powder particles to have an average particle size smaller than that of the conventional ferrite particles. The present invention
20 has been accomplished based on this discovery.

Namely, the present invention provides a magnetic carrier powder composed of ferrite powder particles having a spinel structure and an average particle size of less than 30 μm .

There has hitherto been no instance where ferrite powder
5 particles having such a small particle size have been used alone as a carrier.

Now, the present invention will be described in detail with reference to the preferred embodiments.

The magnetic carrier powder of the present invention is made of
10 a ferrite having a spinel structure.

As the ferrite having a spinel structure, there may be mentioned a so-called soft ferrite such as a 2-3 spinel or a 1-3 spinel, a magnetite (Fe_3O_4) or a maghemite ($\gamma\text{-Fe}_2\text{O}_3$).

Among these ferrites, the following ferrites i) and ii) are
15 particularly preferred in view of its magnetic characteristics.

i) a spinel ferrite comprising at most 60 molar % of MO where M is Ni, Mn, Mg, Zn, Cu, Co or a combination thereof, as calculated as a divalent oxide, and at least 40 molar % of Fe_2O_3 as calculated as a trivalent metal oxide.

20 In this case, when M is a combination of at least two kinds of metals, their proportions may be optionally selected.

ii) a magnetite.

Among the ferrites i), the following ferrites ia) and ib) are preferred.

25 ia) a ferrite i) wherein M is Ni, Mn, Mg, Cu, Zn or a combination thereof. In this case, when M is a combination of at least two kinds of metals, their proportions may be optionally selected.

ib) a ferrite i) wherein M is a combination of Ni, Mn, Mg, Cu,

Zn or a combination thereof, with at most 20 atom % of Co.

In this case, when M is a combination of at least two kinds of metals selected from Ni, Mn, Mg, Cu and Zn, their proportions may be optionally selected.

5 When such a ferrite (a) or (b) is used, the saturation magnetization becomes extremely high, whereby the deposition of the carrier on the photosensitive material or scattering of the carrier from the magnetic brush can be minimized.

10 The ferrite powder particles having the above-mentioned composition may further contain at most 5 molar % of an oxide of Ca, Bi, Cr, Ta, Mo, Si, V, B, Pb, K, Na, or Ba.

Such ferrite powder particles have an average particle size of less than 30 μm .

15 If the average particle size is 30 μm or greater, the image quality, particularly the resolving power, graininess, uniformity or gradation tends to be degraded. Further, the image quality tends to be of high contrast, which taxes the eyes of the observer.

20 On the other hand, if the average particle size is too small, the deposition of the carrier particles on the photosensitive material or the scattering of the carrier tends to be pronounced and the flowability of the developer tends to be poor. Therefore, the average particle size should preferably be at least 5 μm . Particularly good results are obtainable when the average particle size is from 5 to 25 μm .

25 Further, the particle size distribution is usually such that about 70% of the total particles have a particle size falling within the range of $\pm 30\%$ of the average particle size.

Such ferrite particles are used as a carrier without being coated with a coating layer on the surfaces or without being dispersed in a resin. Therefore, the magnetic carrier powder of the present invention has great mechanical strength and hardly undergoes thermal degradation, whereby the degradation of its properties with time is minimum and its useful life is very long. Further, the reduction of the saturation magnetization due to the decrease of the volume occupying rate is minimum and its production is quite easy.

The ferrite powder particles constituting the magnetic carrier powder of the present invention preferably have an electric resistance of from 10^4 to $10^{14} \Omega$, more preferably from 10^5 to $10^{12} \Omega$, when 100 V is applied in the following manner.

Namely, the measurement of the electric resistance of the ferrite powder particles is conducted in the following manner in accordance with a magnetic brush development system. An N-pole and a S-pole are arranged to face each other with a magnetic pole distance of 8 mm so that the surface magnetic flux density of the magnetic poles becomes 1500 Gauss and the surface area of the facing poles is 10 x 30 mm. Between the magnetic poles, a pair of flat non-magnetic electrodes are disposed in parallel to each other with an electrode distance of 8 mm. Between the electrodes, 200 mg of a test sample is placed and the sample is held between the electrodes by the magnetic force. With this arrangement, the electric resistance is measured by an insulation resistance tester or an ampere meter.

If the electric resistance as measured in such a manner exceeds $10^{14} \Omega$, the image density tends to be low. On the other hand, if the resistance is less than $10^4 \Omega$, the image quality tends to be of high contrast.

Further, in the present invention, the saturation magnetization σ_m of the ferrite particles is preferably at least 35 emu/g, whereby the deposition of the carrier on the photosensitive material or the scattering of the carrier by repeated development operations can be minimized. In this case, better results are obtainable when the saturation magnetization σ_m is at least 40 emu/g.

The magnetic carrier powder composed of such ferrite powder particles may be prepared in such a manner as disclosed in U. S. Patent No. 3,839,029, No. 3,914,181 or No. 3,926,657.

Namely, firstly, the corresponding metal oxides are mixed. Then, a solvent such as water is added and the mixture is slurried, for instance, in a ball mill. Other additives such as a dispersing agent and a binder may be added as the case requires. Then, the slurry is granulated and dried by a spray drier. Thereafter, the granules thereby obtained are burned at a predetermined burning temperature in a predetermined burning atmosphere. The burning is conducted in a fluidized furnace, a rotary kiln or a tunnel furnace, whereby particles having the above-mentioned average particle size is efficiently produced. After the burning, the particles are pulverized or dispersed to obtain a desired particles size, whereby the magnetic carrier powder of the present invention is obtained.

The magnetic carrier powder of the present invention is mixed with a toner to obtain a developer. In this case, the type of the toner to be used is not critical and any toner may be used. Further, the magnetic brush development system and the photosensitive material to be employed to obtain an electrostatic copy image are not critical and an electrostatic copy image can be obtained

in accordance with a conventional magnetic brush development method.

According to the present invention, an extremely good image quality is obtainable. Namely, the resolving power, graininess, black uniformity and gradation thereby obtained are extremely good. The image is of soft gradation, which does not very much tax the eyes of the observer.

Further, the composition of the ferrite powder particles or the conditions for the burning may readily be varied to optionally change the quantity of magnetism or electric resistance so that images having various image densities and gradations may readily be obtained.

Further, the ferrite powder particles do not have a coating layer or they are not incorporated in a resin. Therefore, the degradation of the characteristics is minimum even when they are used for a long period of time, and they have good durability and a long useful life. They are free from the reduction of the magnetic characteristics which is likely to be led when incorporated with a resin component. Further, the number of the steps for their production can be minimized and the production is easy, whereby the production costs will be low.

Now, the present invention will be described in further detail with reference to Examples.

EXAMPLES:

Metal oxides were mixed at various ratios (calculated as a divalent metal oxide and Fe_2O_3) as shown in Table 1.

One part by weight of water was added to one part by weight of each mixture and mixed in a ball mill for five hours to obtain a slurry. Appropriate amounts of a dispersing agent and a binder were added.

Then, the slurry was granulated and dried at a temperature of at least 150°C by a spray drier.

Each granular product was burned in a fluidized furnace at the maximum temperature as shown in Table 1 in the atmosphere also as shown in Table 1. In Table 1, A represents an air atmosphere and N represents a nitrogen atmosphere.

Thereafter, the granules were pulverized and classified to obtain ferrite powder particles having the average particle size as shown in Table 1. The average particle size is an average particle size of 5000 particles randomly selected under observation by an electron microscope. In the Table, the average particle size of 20 μm indicates that the particles have a particle size within a range of from 5 to 30 μm ; the average particle size 40 μm indicates that the particles have a particle size within a range of from 25 to 55 μm ; and the average particle size of 70 μm indicates that the particles have an particle size within the range of from 40 to 100 μm .

On the other hand, each powder of the ferrite powder particles was subjected to an X-ray analysis, whereby it was confirmed that each powder had a spinel structure and the metal contents corresponding to the feed composition as shown in Table 1.

5 Then, the saturation magnetization σ_m (emu/g) of each powder of the ferrite powder particles and the electric resistance (Ω) under application of 100 V were measured. The results thereby obtained are shown in Table 1. The saturation magnetization σ_m was measured by magnetometer of a sample vibration type.

10 The electric resistance was obtained by measuring electric resistance of the samples of 200 mg by application of 100 V in the aforementioned manner by an insulation resistance meter.

Table 1

Sample No.	Feed composition (molar %)	B u r n i n g		Average particle size (μm)	Saturation magnetization σ_m	Electric resistance [at 100V 200g] (Ω)
		Maximum temperature ($^{\circ}\text{C}$)	Atmosphere			
1	$(\text{FeO})_{50}(\text{Fe}_2\text{O}_3)_{50}$	1350	N	20	85	10^7
2	$(\text{MgO})_{20.5}(\text{CuO})_{7.5}(\text{ZnO})_{20}(\text{Fe}_2\text{O}_3)_{62}$	1300	A	70	62	10^9
3	"	"	"	40	61	10^9
4	"	"	"	20	58	10^{10}
5	$(\text{MnO})_{20}(\text{MgO})_{15}(\text{ZnO})_{18}(\text{Fe}_2\text{O}_3)_{47}$	1300	A	20	40	10^{12}
6	$(\text{MnO})_{23}(\text{CuO})_{7.5}(\text{ZnO})_{20}(\text{Fe}_2\text{O}_3)_{49.5}$	1250	A	20	45	10^9
7	$(\text{MnO})_{27}(\text{ZnO})_{20}(\text{Fe}_2\text{O}_3)_{53}$	1320	N	40	72	10^8
8	"	"	"	20	70	10^9
9	$(\text{ZnO})_{20}(\text{Fe}_2\text{O}_3)_{80}$	1350	N	20	95	10^6
10	$(\text{NiO})_{32}(\text{CuO})_1(\text{ZnO})_{15}(\text{MnO})_{2.5}(\text{Fe}_2\text{O}_3)_{49.5}$	1260	N	20	45	10^8
11	$(\text{MgO})_{21}(\text{CuO})_4(\text{ZnO})_{20}(\text{CoO})_5(\text{Fe}_2\text{O}_3)_{50}$	1280	A	20	45	10^{10}
12	$(\text{MgO})_{13.5}(\text{CuO})_{7.5}(\text{ZnO})_{20}(\text{Fe}_2\text{O}_3)_{60}$	1280	A	20	48	10^9

Each ferrite powder thus obtained was used by itself as a magnetic carrier powder. Namely, it was mixed with a commercially available two-component toner (an average particle size of $11.5 \pm 1.5 \mu\text{m}$) to obtain a developer having a toner concentration of 11.5% by weight.

5 With use of each developer, magnetic brush development was carried out by means of a commercially available electrostatic copying machine and the image quality of the image thereby obtained was evaluated. In this case, the surface magnetic flux density of the magnetic roller for the magnetic brush development was 1000 Gauss;
10 the rotational speed of the magnetic roller was 130 rpm and the rotational speed of the sleeve roller was 30 rpm. Further, the space between the magnet roller and the photosensitive material was 3.0 ± 0.3 mm. As the photosensitive material, a CdS photosensitive material of binder type was used and the maximum surface
15 electric potential was 800 V.

The resolving power (lines/mm) was measured by means of a test chart made by Data Quest Company. The image of the test chart was observed by naked eyes to evaluate the graininess. The evaluation was made in accordance with five ratings A to E
20 where A represents the best and E represents the worst.

Further, the gradation was evaluated by observation with naked eyes. The evaluation was made by means of a grade scale comprising 13 grades and the expressed by the grade numbers (1-13).

The soft gradation was evaluated also by observation with
25 naked eyes. In this case, the order of superiority was expressed by a number.

The results thereby obtained are shown in Table 2.

0086444

- 11 -

With each sample, the deposition of the carrier on the photo-sensitive material and the scattering of the carrier were extremely small.

Table 2

Sample No.	Resolving power (lines/mm)	Graininess	Gradation	Soft gradation
1	6.3	A	10	1
2(Comparative)	4.0	E	6	3
3(Comparative)	4.5	C	6	3
4	6.3	A	10	1
5	6.3	B	11	1
6	6.3	A	10	1
7(Comparative)	4.5	D	6	3
8	6.3	A	10	1
9	5.6	A	8	2
10	6.3	A	10	1
11	6.3	A	10	1
12	6.3	A	10	1

From the results shown in Table 2, it is evident that the magnetic carrier powders of the present invention give far superior electrostatic images to those having an average particle size of at least 30 μm .

CLAIMS:

- 1) A magnetic carrier powder composed of ferrite powder particles having a spinel structure and an average particle size of less than 30 μm .
- 5 2) The magnetic carrier powder according to Claim 1 wherein the ferrite powder particles are made of a soft ferrite selected from 2-3 spinel and 1-3 spinel ferrites, a magnetite or a maghemite.
- 3) The magnetic carrier powder according to Claim 1 wherein the ferrite powder particles are made of a spinel ferrite comprising at
10 most 60 molar % of MO where M is Ni, Mn, Mg, Zn, Cu, Co or a combination thereof, as calculated as a divalent metal oxide, and at least 40 molar % of Fe_2O_3 as calculated as a trivalent metal oxide.
- 4) The magnetic carrier powder according to Claim 1 wherein the ferrite powder particles are made of a magnetite.
- 15 5) The magnetic carrier powder according to Claim 3 wherein M is Ni, Mn, Mg, Cu, Zn or a combination thereof.
- 6) The magnetic carrier powder according to Claim 3 wherein M is a combination of Ni, Mn, Mg, Cu, Zn or a combination thereof, with at most 20 atom % of Co.
- 20 7) The magnetic carrier powder according to Claim 3 wherein the spinel ferrite contains at most 5 molar % of an oxide of Ca, Bi, Cr, Ta, Mo, Si, V, B, Pb, K, Na or Ba.
- 8) The magnetic carrier powder according to Claim 1 wherein the average particle size is within a range of from 2 to 25 μm .
- 25 9) The magnetic carrier powder according to Claim 1 wherein the ferrite powder particles have a particle size distribution such that at least 70% of the particles have a particle size within a range of $\pm 30\%$ of the average particle size.
- 10) The magnetic carrier powder according to Claim 1 wherein the
30 ferrite powder particles have an electric resistance ρ from 10^4 to

$10^{14} \Omega$, preferably from 10^5 to $10^{12} \Omega$, when 100 V is applied.

11) The magnetic carrier powder according to Claim 1 wherein the ferrite powder particles have a saturation magnetization σ_m of at least 35 emu/g.



European Patent
Office

EUROPEAN SEARCH REPORT

0086444

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 83101193.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	DE - A - 2 261 183 (THOMSON-CSF) * Claims 1,2 *	1	H 01 F 1/36 G 03 G 9/10 C 04 B 35/26
D,A	US - A - 3 929 657 (JONES) * Totality *	1-3,5,6	
A	US - A - 4 042 518 (JONES) * Claim *		
A	EP - A1 - 0 010 732 (TDK ELECTRONICS) * Claims; examples *	1-3,5,6	
A	GB - A - 751 623 (STEATITE RESEARCH CORPORATION) * Totality *	1-3,5,6	TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
A,P	DE - A1 - 3 132 494 (COMPAGNIE INTERNATIONALE) * Claims 1,2 *	1-3,5,6	H 01 F 1/00 G 03 G 9/00 C 04 B 35/00 G 11 B 5/00
A	DE - A - 2 359 424 (MONTECATINI) * Pages 3,4 *	1	
A	DE - B2 - 1 449 403 (N.V. PHILIPS)		
A	US - A - 3 509 058 (GEORGES ESTIVAL)	1-3,5,6	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 21-05-1983	Examiner TSILIDIS
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			



European Patent
Office

EUROPEAN SEARCH REPORT

0086444
Application number

EP 83101193.7

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,A	<u>US - A - 3 839 029</u> (BERG et al.) --		
D,A	<u>US - A - 3 914 181</u> (BERG et al.) ----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)